The Influence of Physical Conditions on the Velocity of Decomposition of certain Crystalline Solids.

By C. N. Hinshelwood, B.A., Fellow of Balliol College, and E. J. Bowen, B.A., Balliol College.

(Communicated by Prof. F. A. Lindemann, F.R.S.   Received February 25, 1921.)

The study of the velocity of chemical change has usually been confined to substances in the liquid or gaseous state. The temperature coefficient of the velocity is of special importance, since it can be used to calculate the " critical increment " or ' heat of activation " of the reacting molecule. In the case of reactions in solution the velocity is very largely influenced by the solvent, but the quantitative relationships do not conform to any simple law, owing to such factors as the formation of molecular complexes.

Reactions in the solid state have not been much studied, although in many respects the solid state is simpler, owing to the fixed arrangement of the atoms in a space lattice. The object of the experiments described in this paper was to ascertain whether simple quantitative relationships could be found for cases of "irreversible" decompositions of certain crystalline solids. The results show that in these cases the temperature coefficient is a complicated quantity, dependent on several physical factors ; and that the heat of activation cannot be calculated from it. On the other hand, a simple relation is found connecting the rate of evolution of oxygen from solid solutions of potassium permanganate in potassium perchlorate and the heats of activation of the potassium permanganate in the various solid solutions.

It was shown in a previous paper[*] that potassium permanganate decomposes more slowly in solid solution in potassium perchlorate than in the pure state. According to the accepted view,[†] a molecule only decomposes when it possesses a sufficient excess of energy over the mean energy corresponding to the temperature of the system to which it belongs. This is the " heat of activation " and per gramme-molecule is identical with the quantity Q in Trautz's theorem, which represents the velocity constant k of a chemical change by an exponential function of the form

$$k = \chi e^{-Q/RT} \text{ where } \chi = \text{constant.}$$

If the heat of activation, Q, be modified by an amount q, then k will be changed to a value k' given by

$$ln \frac{k}{k'} = \frac{q}{RT}. \tag{1}$$

[*] ' Phil. Mag.,' vol. 40, p. 569 (1920).
[†] E.g., Lewis, ' J.C.S.,' vol. 109, p. 796 (1916).

As an element of the permanganate crystal structure—presumably the MnO$_4$ ion—becomes more stable when placed in a lattice consisting partly of perchlorate, it may be assumed that the heat of activation increases. If we assume that the difference in the heats of activation of potassium permanganate caused by a difference in its surroundings is equal to the heat given out when passing from one surrounding to another, the relative rates of decomposition in different solid solutions can be calculated from the heats of mixture of potassium perchlorate and permanganate in the solid state. These can be obtained from measurements of Sommerfeld, and calculation of the decomposition velocities from these data has been found to agree with direct measurement, as described in § 4.

Before this result could be obtained, however, a number of points connected with the dynamics of solid reactions had to be cleared up. In the first place, we have already shown (*loc. cit.*) that the decomposition by heat of crystalline substances, such as potassium permanganate and ammonium bichromate, takes place only on the surface of the crystals. Hence in any comparative experiments it is necessary to control the surface. It is found (§ 3) that the surface determining the velocity of reaction is considerably greater than the apparent surface deduced from the linear size of the crystals, since what is apparently a single crystal really consists of discontinuous aggregates.

The second complication relates to the fact that the surface may increase very greatly as the reaction proceeds, owing to the disintegration of large crystals. This was shown previously to occur with large crystals of potassium permanganate, the decomposition of which proceeds with a very marked acceleration. The acceleration largely disappeared when the crystals were ground up initially. The effect is illustrated by experiments on silver permanganate, described in § 1.

Another effect is sometimes observed in the early stages of the reaction in cases where the products form a coherent film on the surface of the crystal, the reaction being checked as soon as the surface has become completely covered with this film. We have therefore to consider not only the progress of the reaction with time, but its propagation into the interior of the crystal (§ 2). This complication, together with the fact that the effective surface may vary with temperature, renders the temperature coefficient useless for determining the heat of activation.

§ 1.—*Accelerated Decomposition (of Silver Permanganate).*

This substance evolves oxygen at a much lower temperature than the potassium salt, and measurements could be made at $110.0°$ C. The experi-

mental method consisted in heating in a vapour bath about 0·5 grm. of the substance, contained in a small bulb and connected by a capillary tube with a gas-measuring burette. Small but well-formed crystals, whose mean longer axis was 0·25 mm. and whose shorter axis was on the average 0·027 mm., decomposed in a markedly accelerated manner, while when these were ground so that the mean diameter of the particles was about 0·005 mm. the initial rate was much increased and the acceleration very considerably diminished. The following results represent the mean of two concordant experiments in each case :—

Percentage of Total Oxygen evolved during Successive
Periods of 30 minutes at 110·0° C.

	Crystals.	Powder.
0– 30 minutes	4 ·0	25 ·5
30– 60 ,, ...	4 ·0	40 ·0
60– 90 ,, ...	13 ·5	29 ·5
90–120 ,, ...	30 ·5	10 ·0
120–150 ,, ...	23 ·0	3 ·0

§ 2.—*Propagation of the Reaction from the Surface into the Interior.*

When a crystal decomposes, the change commences on the surface and is gradually propagated into the interior. It must be clearly understood that the process here referred to is an isothermal one, time having been allowed for the crystal to attain a uniform temperature throughout its mass. If the products of reaction do not form a coherent film, the change proceeds without hindrance, and, as already stated, may be strongly accelerated owing to the disintegration of the crystal. An experiment was previously described in which a large crystal of ammonium bichromate was allowed to decompose at 212° C. When the surface had become covered with a film of chromium oxide the gas evolution was checked. The effect is well seen by crushing a crystal in this state. With light pressure the fragments are all found to be covered with the black layer; further crushing shows the interior of the particles to be undecomposed.

Measurements made at a series of temperatures have now shown that as the temperature increases this retardation becomes less and less marked, and is succeeded by the usual type of accelerated reaction. The curves in fig. 1 show the results of a series of experiments with small crystals of ammonium bichromate. The substance was heated in glass vessels of about 10 c.c. capacity, connected with a mercury manometer, whereby the pressure developed was measured, the volume being maintained constant. Since water

vapour is given off during the decomposition, the arrangement of the apparatus also ensured that the whole of the decomposition vessel was at the temperature of the vapour bath.
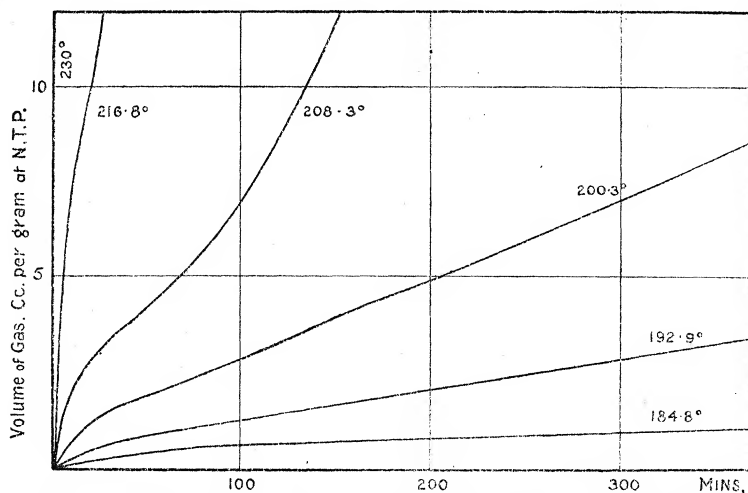

Fig. 1.—Decomposition of Ammonium Bichromate.   Initial Stages.

If the times necessary for a given amount of gas evolution to occur at two different temperatures are compared, it is clear that the tendency of the retardation to disappear at the higher temperatures may give rise to what is apparently an abnormally high temperature coefficient. For example, the time required for the evolution of 1 c.c. per gramme at 200·3° C. was 18 minutes, while at 184·8° C. it was 330 minutes. Expressed in the conventional way, this means a temperature coefficient of 6·5 for 10°, which is much higher than is ever found for a homogeneous reaction. The abnormally high value results from the fact that not only does the reaction velocity increase as the temperature rises, but the reaction is also propagated more easily into the interior.

With potassium permanganate this effect is not observed, since the products are not firmly retained, but in the initial stages of the decomposition of the solid solutions in potassium perchlorate a retardation may be observed, because here the decomposition products are more or less firmly held by the surrounding structure. Fig. 2B illustrates the transition from the accelerated initial change of pure permanganate to the retarded decomposition of the dilute solid solutions. Solid solutions containing about 60 per cent. of potassium permanganate give an almost linear relationship between time and percentage decomposition. The results plotted in these curves were obtained with material ground as nearly as possible to the same state of subdivision.

Increase of temperature, as well as decrease in size of particles, renders the propagation into the interior easier, as may be seen from fig. 2A which represents the initial rates of decomposition of a single solid solution at various temperatures.
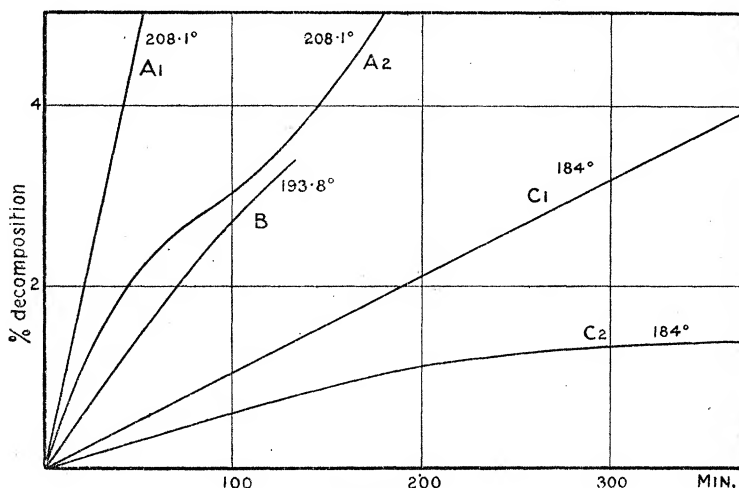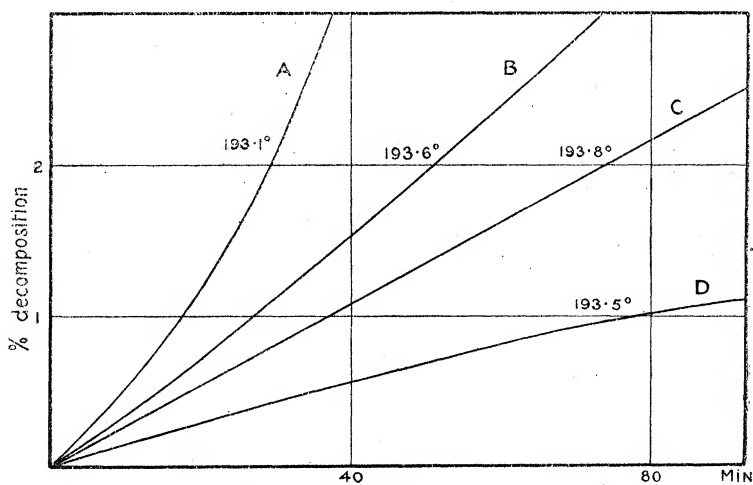

FIG. 2A.

FIG. 2B.

FIG. 2A.—Solid Solution containing 60·5 per cent. KMnO$_4$. A1, B, C1, finely ground. A2, C2, small crystals.

FIG. 2B.—Solid Solutions of various Compositions. A, 100 per cent. KMnO$_4$. B, 76·5 per cent. KMnO$_4$. C, 60·5 per cent. KMnO$_4$. D, 24·7 per cent. KMnO$_4$.

§ 3. *Influence of the Size of Particles on the initial Rate of Reaction.*

While it is quite clear qualitatively that the rate of reaction increases with the degree of subdivision, the exact relation between rate and crystal size requires further consideration. If a given mass of substance the mean linear magnitude of whose particles is a be subdivided into particles whose mean linear magnitude is b, then the surface is increased in the ratio a/b. But experiment shows that the velocity of reaction does not increase in this ratio, but in a considerably smaller one. This implies that the surface which is effective in determining the rate of reaction is considerably greater than the apparent surface as deduced from the linear size of the particles. What appears to be an individual crystal is really composed of aggregates, some of which are sufficiently loosely held together to allow decomposition to take place between them. This is in accord with the results derived from the consideration of tensile strength, which is always much lower than would be expected if the material were continuous. From this it is concluded that the tensile strength represents the force between small aggregates.

The following is a typical result :—

Solid solution of $KMnO_4$ in $KClO_4$,

60·6 molecular percentage.

Mean diameter of particles.	Initial rate of decomposition at 184·3 C.
0·38 mm.	0·0054 per cent. per min.
0·026 mm.	0·0106 per cent. per min.

The ratio of the velocities is 1·96.

At 208·1° C. the ratio was found to be 2·13. Taking the mean as 2·05, it is seen that this is considerably less than the inverse ratio of the linear sizes $0·38/0·026 = 15$.

§ 4.—*The Evolution of Oxygen from Isomorphous Mixtures of Potassium Permanganate and Perchlorate. Dependence of Reaction Velocity on the Concentration of Potassium Permanganate.*

It may be stated at the outset that at the temperature of the experiment only the potassium permanganate undergoes measurable decomposition. Nevertheless, the stability of the permanganate elements of the crystal structure is influenced by the presence of the perchlorate elements. It is, therefore, of interest to determine the velocity of oxygen evolution from solid solutions of various compositions.

It is clear that to find out how the stability of the potassium permanganate crystal element depends on its environment, the decomposition should

only be measured in its initial stages, since if it be allowed to proceed to a more advanced stage complications may occur, due to the varying facility with which the change is propagated into the interior of the crystals of different compositions. In the different experiments of a series it is necessary to use crystals which possess the same surface. This is difficult, since the apparent surface is not a real index of the true surface. One must, however, employ crystals of the same apparent size and regard the results as partly statistical.

The determination of the initial velocities was attempted by two methods. The first was to follow the decomposition to about 5 per cent. and determine the initial rate directly. The second was to follow the decomposition over its whole course and to extrapolate. But the changes in curvature near the commencement are so marked that the extrapolation must be regarded as rather arbitrary.

The experimental method consisted in heating in a vapour-bath about 0·5 grm. of the substance contained in a small glass bulb, and connected by a capillary tube to a mercury manometer in the first series and to a small gas-burette in the second. The oxygen evolved was thus measured, either by increase in pressure in the apparatus, or by direct reading of its volume under atmospheric pressure.

The following results were obtained. (The figures represent initial velocities in per cent. per minute) :—

Temp.	Mol. p.c. $KMnO_4$. 100 p.c.	Temp.	Mol. p.c. $KMnO_4$. 76·5 p.c.	Temp.	Mol. p.c. $KMnO_4$. 60·5 p.c.	Temp.	Mol. p.c. $KMnO_4$. 58·5 p.c.
148·0	0·00185	182·3	0·0185	184·3	0·0106	182·3	0·0038
183·4	0·0295	193·2	0·042	193·8	0·0270	192·7	0·0138
192·3	0·0550			208·1	0·103	206·2	0·056
193·1	0·053						
Value deduced for 200° 0·091.		Value deduced for 200° 0·070.		Value deduced for 200° 0·048.		Value deduced for 200° 0·029.	

Temp.	Mol. p.c. $KMnO_4$. 46·2 p.c.	Temp.	Mol. p.c. $KMnO_4$. 33·5 p.c.	Temp.	Mol. p.c. $KMnO_4$. 24·7 p.c.	Temp.	Mol. p.c. $KMnO_4$. 24·3 p.c.
193·5	0·035	193·2	0·024	207·2	0·056	229·3	0·39
				230·2	0·38		
Value deduced for 200° 0·059.		Value deduced for 200° 0·042.		Value deduced for 200° 0·031.		Value deduced for 200° 0·034.	

The effect of temperature varies from one solid solution to another. This must be attributed to a greater or lesser loosening of the crystal aggregates

as the temperature rises. For this and the other physical reasons previously discussed, it is of little value to calculate the "heat of activation" from the temperature coefficient.

From these results the following series of relative values at 200° C. is found by plotting the logarithm of the initial rate against temperature.

Molecular percentage KMnO$_4$.	Relative initial velocity.
100·0	100
76·5	77
60·5	53
58·5	32
46·2	65
33·5	46
24·7	34
24·3	37

In fig. 3, the curve B is drawn in the most probable position through these points. Considerable deviations from the mean are to be expected owing to variations in the effective surface.
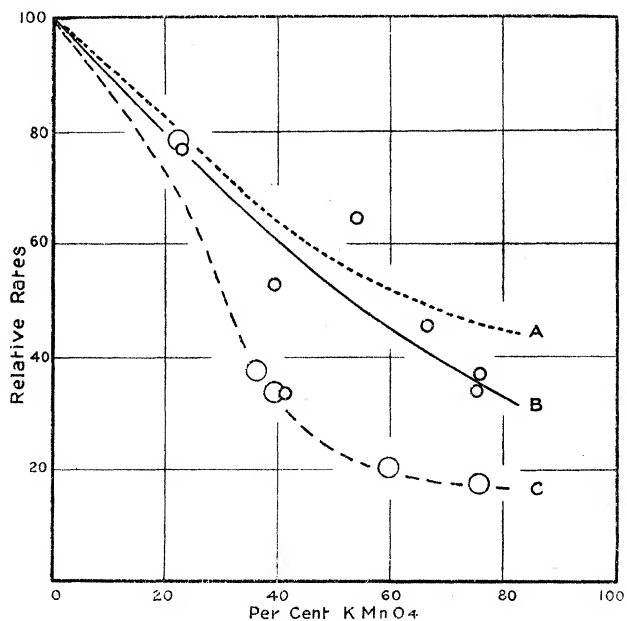

FIG. 3.—Relative Velocities of Decomposition of Solid Solutions of KMnO$_4$ in KClO$_4$ at 200°. A, Initial Rates calculated from heat of mixture. B, Initial Rates observed. C, Rates estimated arbitrarily from times required for 20 per cent. decomposition.

In the second series the whole course of the change was followed at 240° C. small crystals selected by sieving being used. The relative velocities as deduced from the times required for 20 per cent. decomposition are given below and in the curve C in fig. 3. This curve is steeper than A owing to the physical cause already discussed.

Molecular percentage KMnO₄.	Relative velocity.
100·0	100
76·5	79
63·0	38
60·5	34
40·8	21
24·7	18

From the curve of initial velocities (curve B) in fig. 3 we can test equation (1) according to which if the heat of activation is increased by q the velocity constant is reduced from k to k' where

$$ln \frac{k}{k'} = \frac{q}{RT}.$$

Putting initial velocities proportional to k we have, for an *equimolecular mixture* at 200°,

$$\frac{k}{k'} = \frac{100}{52},$$

whence

$$ln \frac{100}{52} = \frac{q}{1 \cdot 98 \times 473},$$

∴ $q = 618$ calories per gramme molecule KMnO₄,

or   309 calories per gramme molecule of the equimolecular mixture.

This has been assumed equal to the heat of solid mixture.

This heat of solid mixture can be determined directly from the heats of solution of potassium permanganate, perchlorate and the mixed crystals. E. Sommerfeld* has determined these accurately, and from his results it is clear that there is a small evolution of heat when mixing takes place in the solid state. For 1 gramme molecule of the equimolecular mixture it amounts to 260 calories. Since this represents the difference between heats of solution which amount separately to about ten thousand calories, better agreement cannot be expected, with the value estimated above. Moreover, these measurements were made about 180° below those of the reaction velocities, so that a comparison implies that the specific heats of the solid solution can be calculated additively from those of the components.

* 'Neues Jahrbuch für Mineralogie,' Beilage Band XIII, p. 443 (1900).

From a curve of Sommerfeld's results the following heats of mixture per gramme molecule of potassium permanganate are deduced :—

	Per cent.	Per cent.	Per cent.	Per cent.
$KMnO_4$	80	60	50	40
$KClO_4$	20	40	50	60
Calories	159	403	520	600

Using equation (1), we may calculate from these figures the relative rates of decomposition of potassium permanganate in solid solutions of various compositions. These are shown in curve A in fig. 3, and it will be seen that the theoretical curve lies very close to the curve B, representing the experimental results. From this it is clear that the lowering in velocity is explained by the change in heat of activation being equal to the heat of solid mixture.

The results described in this paper once more seem to confirm the view that no distinction can be drawn between physical and chemical forces. The chemical forces between the atoms of solid substances are profoundly modified by physical conditions, such as proximity to the surface, and by the presence of neighbouring atoms in the space lattice. Moreover, the decrease in potential energy attending the physical process of solid mixture leads directly to increased chemical stability in a way which can be calculated approximately from the heat of mixture. It will be interesting to see whether similar agreement can be found in the case of other isomorphous mixtures, including those with a negative heat of formation.